18 (**2a**) and 50 (**2b**) h in the presence of a catalytic amount of the complex $ZnCl_2$–1-phenylethylamine by using a Dean–Stark device for water separation.

***N*-(1-Phenylethyl)-1-phenylethanimine (2a)**: bp 123 °C (1.0 mm); yield, 85%; IR $\nu_{max}$ (neat) 1635 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.50 (d, $J$ = 7 Hz, $CH_3CH$), 2.10 (s, $CH_3C{=}N$); 4.80 (q, $J$ = 7 Hz, $CHCH_3$); 7.30 (m, Ar); $^{13}C$ NMR ($CDCl_3$) $\delta$ 162.79 (C=N), 59.14 (CHMePh), 24.83 (*Me*CHPh), 15.10 (*Me*C=N); $^{13}C$ NMR ($CD_3OD$) $\delta$ 145.60 ($C{=}CD_2$), 60.60 ($CD_2{=}C$), 59.69 (CHMePh), 24.05 ($CH_3CHPh$).

***N*-(1-Phenylethyl)-1-phenyl-2-methylpropanimine (2b)**: bp 121 °C 0.4 mm); yield, 52%; IR $\nu_{max}$ (neat) 1635 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.10 (d, $J$ = Mz, $CH_3CH$), 1.15 (d, $J$ = 7 Hz, $CH_3CHCH_3$), 1.20 (d, $J$ = 7 Hz, $CH_3CHCH_3$), 2.70 (septet, $J$ = 7 Hz, $CH_3CHCH_3$), 4.20 (q, $J$ = 7 Hz, CHN), 7.15 (m, Ar); $^{13}C$ NMR ($CDCl_3$) $\delta$ 174.06 (C=N), 60.22 CHMePh), 39.09 (CHC=N), 25.04 (*Me*CHPh), 20.13 ($CH_3CHCH_3$); $^{13}C$ NMR ($CD_3OD$) $\delta$ 177.41 (C=N); 61.17 (CHMePh), 39.93 (CHC=N), 24.28 (*Me*CHPh), 20.41 ($CH_3CHCH_3$).

**Mutarotation Experiments.** A Perkin-Elmer 141 polarimeter was used. The temperature was maintained constant to ±5 °C. Imine concentration was chosen to make the range of rotations as large as possible.

**NMR Measurements.** $^1H$ NMR. A Varian T-60 spectrometer was used. The temperature was maintained within ±3 °C. The disappearance of the signal due to the methyl group was measured by double integration on the spectrum conveniently enlarged.

$^{13}C$ NMR. A Varian FT-80 spectrometer was used. The $CD_3OD$ spectra were recorded at least 24 h after solution of the imine.

**Registry No.** 2 (R = Me), 25102-87-8; 2 (R = *i*-Pr), 29412-61-1.

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# Hydrogenation of Nitro Compounds with an Anthranilic Acid Polymer-Bound Catalyst

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Heterogeneous catalysts capable of hydrogenating nitroaromatics are commonplace. In contrast to this, relatively few homogeneous catalysts demonstrate activity with nitro compounds. Among the more successful soluble catalysts are $RuCl_2(PPh_3)_3$[1] and $Co(CN)_5^{3-}$[2] and $RhCl_2(BH_4)(DMF)(py)_2$.[3] An interface area between use of classical heterogeneous catalysts and homogeneous catalysts, involving the use of polymer-bound catalysts, has seen even fewer applications with respect to the hydrogenation of nitro groups. Besides our own reports of nitrobenzene hydrogenation using rhodium[4] or palladium[5] derivatives of anthranilic acid on polystyrene, there seems to be only the report by Jiang and associates.[6] They used a silica-supported polyacrylonitrile complex of palladium.

Here we report more fully the reactions of our palladium derivative of anthranilic acid on polystyrene. We have investigated the hydrogenation of a variety of nitro compounds and have examined steric and electronic effects.

## Results and Discussion

Catalyst preparation for this study is as reported previously.[7] Highly cross-linked polystyrene beads (Rohm and Haas XAD-4) were chloromethylated, the pendant anthranilic acid ligand was attached via substitution, and the ligand beads were treated with palladium chloride (Scheme I).

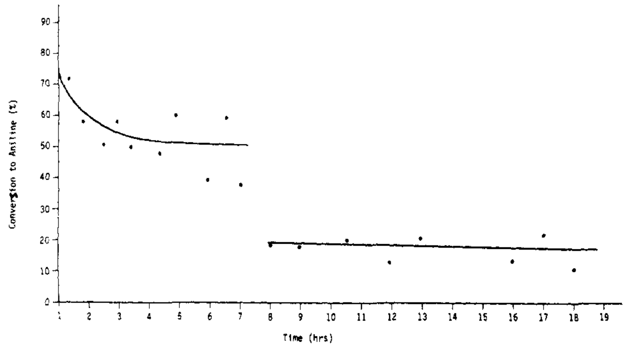
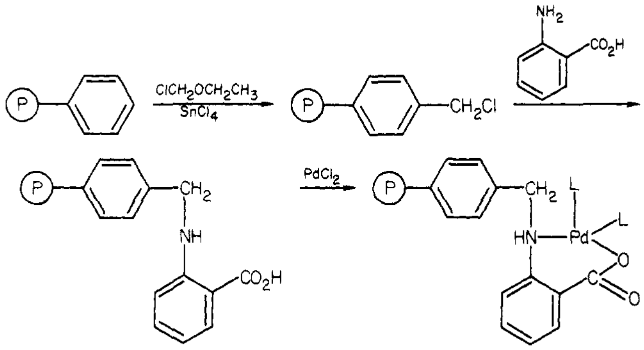


**Figure 1.** Conversion of nitrobenzene to aniline with a flow reactor.

**Scheme I**



Hydrogenation was performed normally at 400–1500 psi and 60–90 °C, though this was a matter of convenience. Nitrobenzene was observed to hydrogenate at room temperature and 60 psi [Table I]. Solvents are not required for liquid aromatic nitrocompounds. The solvents ethanol, ethyl acetate, and glacial acetic acid all result in high amine yields.

In Table I the results of our investigation are summarized. For *p*-chloronitrobenzene it is necessary to perform the reaction at low temperature or the halide is stripped from the ring. The catalyst is not effective for selectively reducing one nitro group in *m*-dinitrobenzene. Other atoms that could coordinate with palladium, as in *p*-nitrophenol and 5-nitroquinoline, do not interfere with the reaction.

The catalyst displays remarkable stability. Nitrobenzene, 20 g (161 mmol) was hydrogenated for 3 h at 100 °C and 500 psi without a solvent, employing 1.00 mmol of catalyst. GC analysis showed the conversion of nitrobenzene to aniline was 76% complete under these conditions. No other products were in evidence. This level of activity represents an average of 40 mol of aniline/mol of Pd/h. The catalyst from this batch run was thoroughly washed with acetone and returned to the reactor and recycled with fresh nitrobenzene; there was a modest drop in activity. After five recycles the activity of the beads had leveled off at 50% of the original activity. The six runs represented a total of 440 mol of aniline/mol of Pd.

The same general performance curve was obtained when a tube reactor was employed. Feeding nitrobenzene at 210 °C under 100 psi of hydrogen, WHSV = 14.3, initially gave

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0022-3263/84/1949-2626$01.50/0

**Table I. Hydrogenation of Nitroaromatics (1 mmol Catalyst)**

| compd | mmol | pressure, psi | time, h | temp, °C | solvent, mL | product(s) (yield, %)[a] |
|---|---|---|---|---|---|---|
| *p*-nitrophenol | 30 | 400 | 15 | 90 | EtOH, 20 | *p*-aminophenol (98) |
| *m*-dinitrobenzene | 60 | 1500 | 1 | 60 | EtOH, 20 | *m*-nitroaniline (1)<br>*m*-phenylenediamine (90) |
| *β*-nitrostyrene | 20 | 400 | 12 | 90 | EtOH, 20; HOAc, 1 | four products (unidentified) |
| 5-nitroquinoline | 3.0 | 1000 | 18 | 50 | EtOAc, 20 | 5-aminoquinoline (55) |
| *o*-nitrotoluene | 15 | 600 | 4 | 100 | EtOAc, 20 | *o*-toluidine (88) |
| *m*-nitrotoluene | 15 | 600 | 4 | 100 | EtOAc, 20 | *m*-toluidine (96) |
| *p*-nitrotoluene | 15 | 600 | 4 | 100 | EtOAc, 20 | *p*-toluidine (80) |
| *p*-chloronitrobenzene | 10 | 600 | 4 | 100 | EtOAc | *p*-chloroaniline (56) |
| nitrobenzene | 20 | 600 | 4 | 100 | | aniline (94) |
| nitrobenzene | 20 | 60 | 48 | 25 | | aniline (66) |

[a] Other products were present in less than 5% amounts.

almost 80% conversion to aniline. The reaction is very clean and the only intermediate seen, present in but trace amounts, was azobenzene. The activity of the catalyst dropped rapidly at first (Figure 1) and then leveled off somewhat. After 6 h of operation the catalyst was washed in the reactor at 100 °C with 95% ethanol. Upon resumption of nitrobenzene hydrogenation the initial activity was lower, but over the course of an additional 10 h of operation there was little further drop in activity. The total average turnovers equaled 900.

A point that should be emphasized from the tube reactor experiment is that XAD-4 beads are reasonably stable at fairly high temperatures. It is generally considered that polymer-bound catalysts cannot be used above 150–160 °C. Indeed this is the case for polystyrenes having a low degree of cross-linking (2%). Such temperature limitations are not observed for highly cross-linked polystyrene such as XAD-4. Thus we have hdrogenated nitrobenzene at 280 °C for 1 h without substantial alteration of bead structure or catalytic activity.

The effects of substituent groups was investigated. The three nitrotoluene isomers (Table I) were hydrogenated at room temperature and 600 psi for 4 h. All three isomers hydrogenated at approximately the same rates. The series *p*-chloronitrobenzene, nitrobenzene, and *p*-nitrotoluene provided a measure of the sensitivity of the reaction to electronic effects. Knifton found that hydrogenation rates were enhanced when electron-withdrawing groups were present.[1c] While conversion of *p*-chloronitrobenzene is somewhat lesser than that for the other nitrocompounds, it is clear the reaction is not highly dependent on electronic effects. The catalyst has an excellent shelf-life. The sample used in this investigation was evaluated over a period of 2 years. There was no measurable loss of activity upon storage at room temperature under air. All manipulations with the catalyst were accomplished without use of an inert atmosphere.

In conclusion, the catalyst is highly active for the hydrogenation of aromatic nitro compounds, has a long lifetime, and displays excellent handling properties.

## Experimental Section

**Materials.** Amberlite XAD-4 was a gift of the Rohm and Haas Co. It was obtained as hard, insoluble 20–50-mesh spheres. The polymer was received wet and was dried in a rotary evaporator at 50 °C for 12 h before being used. Chloromethylation was performed according to the procedure of Pepper et al. In one batch the chlorine content was 1.32% (0.372 mequiv/g).

Anthranilic acid was anchored to the beads by stirring the beads with an excess of anthranilic acid in ethyl ether, acetone, or DMF. The following procedure was typical. To 520 g of the chloromethylated beads suspended in 1 L of ethanol was added 100 g of anthranilic acid. This was refluxed for 20 h, filtered, and washed with 2 L of absolute ethanol at 70 °C. Anal. N, 0.46 (0.33 mequiv/g); Cl, 0.60 (0.169 mequiv/g).

Reagent-grade chemicals were generally used without purification. Duplicate runs were made with bulk-grade benzene and no noticeable initial rate differences were observed.

**PdCl$_2$–Anthranilic Acid Catalyst.** The beads (200 g) were suspended in 500 mL of acetone and 4.2 g (23.4 mmol) of PdCl$_2$ and 5 mL of acetonitrile were added. The suspension was refluxed for 72 h under nitrogen, filtered, washed with acetone, and vacuum-dried. Anal. Pd, 2.05 (0.193 mequiv/g); N, 0.38 (0.271 mequiv/g); Cl, 0.71 (0.200 mequiv/g).

**Instruments and Hydrogenation Procedure.** Low-pressure hydrogenations were carried out in a standard, catalytic apparatus (Parr Instrument Co., Model 3911). In a typical run a 500-mL reactor was charged with unsaturated compound and catalyst and the system was sealed, purged 3 times with hydrogen, and then pressurized to 60 psig. For high-pressure hydrogenation, the reactants were added to the 300-mL reaction vessel of an Aminco Shaking Assembly (No. 44-13106). The reaction vessel was flushed 3 times with hydrogen. For room-temperature reactions the pressure was then adjusted to the desired level. For higher temperature reactions, the reactor was partially pressurized and then heated, with shaking, to the desired temperature. The pressure was then adjusted to the desired level. The reactions were not considered to have begun until the system was at the desired temperature and pressure, and all reaction times were measured from this point. Termination of several experiments at early stages revealed that a low percentage of hydrogenation had occurred.

Infrared absorption spectra were recorded on a Perkin-Elmer 457 spectrophotometer. GLC data were acquired on a Varian Aerograph 1700, using 10% Carbowax or 20% SE-30 columns. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

**Registry No.** *m*-Dinitrobenzene, 99-65-0; *β*-nitrostyrene, 102-96-5; 5-nitroquinoline, 607-34-1; *o*-nitrotoluene, 88-72-2; *m*-nitrotoluene, 99-08-1; *p*-nitrotoluene, 99-99-0; *p*-chloronitrobenzene, 100-00-5; nitrobenzene, 98-95-3.

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# Reaction of α-Terpinene with Methylphosphonous Dichloride[1]

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α-Terpinene (1) is a commercially available cyclohexadiene derivative which we have considered as a possible participant in the McCormack cycloaddition reaction[3] with phosphorus(III) halides. Were this reaction to be

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[2] Shell Division Co., Modesto, CA.

[3] For a recent review, see: Quin, L. D. "The Heterocyclic Chemistry of Phosphorus"; Wiley-Interscience: New York, 1981; Chapter 2.